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13. ABSTRACT (Maximum 200 words) The results of our basic research program on spectroscopy of lithium battery materials are described in this Final Progress Report. As set forth in the original Collaborative Agreement, some of the work was carried out and published jointly with scientists at the Army Research Lab at Fort Monmouth, NJ. Lithium-7 solid state NMR spectroscopy was utilized to characterize the immediate Li ⁺ ionic environment in gel electrolytes prepared by immobilizing liquid electrolytes in a polymer matrix such as poly(acrylonitrile) (PAN) or poly(methylmethacrylate) (PMMA). It was concluded that, although the host polymer does affect the microscopic environment and mobility of the Li ⁺ ions, they are still completely solvated by the liquid solvent molecules in the gel phase. Early in the program, the emphasis on C/Li anodes was shifted to Li insertion transition metal oxide cathodes. We have successfully employed solids state NMR techniques to characterize Li local environment and transport properties in these materials, along with companion studies of the host lattice structure by synchrotron x-ray absorption spectroscopies (EXAFS, NEXAFS). Finally, successful minority student recruitment and mentoring efforts are described (this was a <i>Minority Institution Infrastructure</i> Grant).				
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FINAL PROGRESS REPORT

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- a) "Sodium-23 NMR and Complex Impedance Studies of Gel Electrolytes Based on Poly(acrylonitrile)", with P.E. Stallworth, J. Li, S. Slane, M. Salomon and F. Croce, *Solid State Ionics* 73, 119 (1994).
- b) "Lithium-7 NMR Studies of Gel Electrolytes Based on Poly(methylmethacrylate)", with P.E. Stallworth, F. Croce, S. Slane and M. Salomon, *Electrochimica Acta* 40, 2137 (1995).
- c) "Lithium-7 NMR and X-ray absorption studies of $\text{Li}_{1-x}\text{CoO}_2$ Battery Cathodes", with B. Ouyang, S. Kostov, M. denBoer, X Cao, S. Slane and H.W. Lin, Materials Research Society Symposium on Solid State Ionics IV, *MRS Proceedings*, vol.369, p.59 (1995).
- d) "A Comparative Study of LiMn_2O_4 From Various Sources", with B. Ouyang, M. denBoer, D. Fauteux, A. Massucco, M. vanBuren, M. McLin, *Ibid.*, p.29.
- e) "High Pressure NMR and Conductivity Investigation of PAN-based Gel Electrolytes", with F. Gerace, B. Scrosati J.J. Fontanella, M.C. Wintersgill and C.A. Edmondson, *Solid State Ionics*, in press.
- f) "Investigation of Mixed Cation Effects in $\text{PEO}_9:\text{Cu}_x\text{Zn}_{1-x}(\text{CF}_3\text{SO}_3)$ Polymer Electrolytes", with S. Panero, B. Scrosati, M. Giua and X. Cao, *Solid State Ionics* 83, 73 (1996).
- g) " ^{23}Na NMR Studies of Na_xCoO_2 Cathodes", with P.E. Stallworth, M.M. Doeff, Visco, L. Ping, S.J. Visco, *Solid State Ionics*, in press.
- h) "Impedance and ^7Li NMR Studies of Polymer Electrolytes based on Poly(vinylidene difluoride)", with G.B. Appetecchi, F. Croce, M. Salomon, M. Tavaréz, S. Arumugam, Y. Wang, *Solid State Ionics*, in press.

i) "Electrical Conductivity and $^{6,7}\text{Li}$ NMR Investigation of $\text{Li}_{1+y}\text{CoO}_2$ ", with M. Carewska, S. Scaccia, F. Croce, Y. Wang and S. Arumugam, *Solid State Ionics*, in press.

Submitted

j) "Magnetic Resonance and X-Ray Absorption Investigation of $\text{Li}_x\text{V}_6\text{O}_{13}$ ", with P.E. Stallworth, S. Kostov, M. denBoer and C. Lampe-Onnerud, submitted to *Journal of Applied Physics*.

k) "Electrical, Thermal and NMR Investigation of Composite Polymer Electrolytes Based on PEO, LiI and High Surface Area Inorganic Oxides" with G. Golodnitsky, G. Ardel, E. Shtraus, E. Peled, Y. Dai, Y. Wang and S. Bajue, submitted to *Electrochimica Acta*.

8. SCIENTIFIC PERSONNEL SUPPORTED BY THIS PROJECT:

Dr. Steve Greenbaum (PI - summer salary) Dr. Phil Stallworth and Dr. Bo Ouyang, Dr. Sam Arumugam and Dr. Yinkung Dai (postdocs), Dr. Fausto Croce (visiting scholar), Mr. Xiantao Cao, Mr. Yifeng Wang (Ph.D. students), Mr. Glendon McLachlan, Mr. Jason Marrero and Ms. Maritza Tavarez (M.A. students). All of these people received partial support from the ARO grant with supplemental funds coming from other sources (ONR Grant, internal University and New York State grants). Other students involved in the project but supported solely by other means were Mr. Richner Erisnor and Ms. Sophia Suarez-Gustave (undergraduates) and Mr. Xinghang Zhang (doctoral student).

Degrees awarded during this grant period: Richner Erisnor - BA; Sophia Suarez-Gustave - BA; Cyril Hughes - BA; Glendon McLachlan - MA; Maritza Tavarez - MA; Jason Marrero - MA. Phil Stallworth completed his postdoctoral studies and is now an assistant professor of physics (tenure-track) at the U.S. Naval Academy.

9. REPORT OF INVENTIONS: None

Technical Progress Report - S.G. Greenbaum

Specific aims -

The essential aims have not been modified from the original application, except for the addition of transition metal oxide cathode materials to the research program. The investigation of ion transport processes in gel electrolytes has benefitted from collaborations with several groups, including the lithium battery groups at the Army Research Lab (Dr. Mark Salomon), the University of Rome (Prof. Bruno Scrosati) and Tel Aviv University (Prof. E. Peled). The research on carbon-lithium anode materials has been hampered due to lack of suitable samples, but commitments for obtaining high quality C:Li materials from several sources (Tel Aviv University and Arthur D. Little) are now in place. Although not discussed in the original proposal, we have successfully applied the same spectroscopic tools intended for anode materials to transition metal oxide cathode samples. This change in emphasis is also, in part, justified by the fact that improvements in cathode capacity translate directly to significant enhancement of energy density of the battery, because the cathode can constitute up to 70% of the battery mass.

Results -

Gel Electrolytes

We have shown that gels based on poly(acrylonitrile) or poly(methylmethacrylate) are homogeneous materials, characterized by a single glass transition temperature (T_g). The short range motional processes probed by NMR relaxation measurements are observed to be somewhat different in the gel and liquid electrolyte. That is, gel electrolytes cannot be described as microscopic "pockets" of liquid electrolyte immobilized in a rigid polymer matrix. High pressure NMR and conductivity measurements just completed allow the calculation of activation volumes for ion motion, in much the same way that variable temperature measurements yield activation energies. We found that, although the host polymer impedes ionic motion, activation volumes in gel and liquid electrolytes are essentially the same. Thus it appears that the cations (Li^+ or Na^+) in the gels have essentially the same solvation shell that they do in the liquid electrolytes. The ion transport mechanisms in gels and liquids are therefore similar, in that no direct involvement of the polymer chains in the transport process could be ascertained. However, the presence of the host polymer impedes the ions by increasing the local *microscopic* viscosity (of course the macroscopic viscosity of the gels is very large).

Improvements in lithium ion technology have been recently reported by Bellcore, in which a composite polymer electrolyte based on poly(vinylidene difluoride) (PvDF) was utilized successfully as a replacement for liquid electrolytes employed in the SONY lithium ion technology. Consequently we undertook a study of similar material in collaboration with the polymer electrolyte research group at the University of Rome and the lithium battery group at the Power Sources Division of the US Army Research Laboratory (Fort Monmouth). Our principal findings concerned the relative efficacy of different plasticizer additives and lithium electrolyte salts. The most highly conductive samples were those containing the relatively new lithium methide salt and the DBP plasticizer. Lithium-7 NMR provided information regarding differences in short range ion motion for the different samples. Other additives employed to improve performance are nanocrystalline inorganic oxides such as Al_2O_3 . In another collaborative effort (with Prof. E. Peled of Tel Aviv University in Israel), we investigated composite polymer

electrolytes based on PEO, LiI and inorganic oxides. For materials containing very high salt concentrations (lithium: polymer repeat unit larger than ~ 4), a different ion transport mechanism was noted than in the dilute salt samples.

Transition Metal Oxide Cathodes

While awaiting the arrival of suitable C:Li samples, we became interested in studying the physics and chemistry of Li-intercalation in transition metal oxide cathodes, which is, of course, highly relevant to Li secondary battery research. Through our collaboration with the Power Sources Division of the Army Research Lab (ARL) (which formed the basis of this ARO Cooperative Research Grant), we have obtained a series of variable x (Li-deficient) $\text{Li}_{1-x}\text{CoO}_2$ samples from Alliant Techsystems, Inc. (Horsham, PA). The materials were studied by solid state ^7Li NMR, electron paramagnetic resonance (EPR), and synchrotron x-ray absorption (NEXAFS) of the cobalt K-edge. All techniques combined to give a consistent picture of electron removal that must accompany Li-deintercalation in order to maintain electrical neutrality. To summarize: (i) Stoichiometric LiCoO_2 is diamagnetic but becomes paramagnetic as Li is electrochemically deintercalated. (ii) The compensating electrons come exclusively from the Co d-orbitals, that is, there is no evidence of defect oxide species. (iii) During the early stages of deintercalation, magnetically inequivalent Li-sites can be resolved, demonstrating that deintercalation proceeds non-uniformly at first. Attempts to prepare excess Li samples (i.e. $\text{Li}_{1+x}\text{CoO}_2$) were made in collaboration with the battery research group at the University of Rome. Solid state NMR of both stable isotopes of lithium (^6Li , ^7Li) demonstrated that, in samples containing about 30% excess Li ($x = 0.3$), most of the this excess resides in an impurity phase.

A similar study of $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$ was undertaken in collaboration with Arthur D. Little, Inc. (Cambridge, MA). The most significant result obtained was the unambiguous observation of Mn^{2+} in Li-deficient material. This may be due to a disproportionation reaction [$2\text{Mn}^{3+} \rightarrow \text{Mn}^{4+} + \text{Mn}^{2+}$] which, of course has very serious implications for cycling behavior. These materials appear to cycle extremely well, so further studies are in progress in order to explain the unexpected appearance of Mn^{2+} . Both (Co and Mn oxides) studies were presented as invited papers at the Fall 1994 Materials Research Society Symposium on Solid State Ionics, and were published in the MRS Proceedings.

A collaboration with Uppsala University on $\text{Li}_x\text{V}_6\text{O}_{13}$, where $0 \leq x \leq 6$, was also undertaken. We employed a multitude of spectroscopic techniques, including solid state ^7Li NMR, EPR and synchrotron x-ray absorption (EXAFS and NEXAFS), and succeeded in characterizing the symmetry of the vanadium coordination shell as a function of Li content, and in verifying the vanadium oxidation states deduced by electrochemical titration methods. We found an increase in unit cell size with increasing Li content, which is opposite to the trend observed in other systems such as Li_xCoO_2 .

Minority Student Programs

Because this Cooperative Research Grant was awarded within the context of the *Minority Institution Infrastructure* Program, I will include a summary of our efforts with regard to recruitment and training of minority students during the period covered by this report. (i) Dr. Phillip Stallworth completed an 18-month postdoctoral appointment and is now the only African-

American faculty member of the Physics Department at the U.S. Naval Academy. (ii) Cyril Hughes, a U.S. Navy veteran, completed his B.A. in Physics in June 1995 and is now pursuing an M.S. in Electrical Engineering at New Jersey Institute of Technology. (iii) Glendon McLachlan, a U.S. Marines veteran, completed his M.A. in Physics in June 1995 and is now pursuing a Ph.D. in Biophysics at Albert Einstein College of Medicine. (iv) Maritza Tavaréz completed her M.A. in Physics in June 1996, and is now enrolled in the Astronomy Ph.D. program at the University of Michigan. She is one of fewer than 25 students nationwide awarded an NSF predoctoral fellowship in astronomy. (v) Jason Marrero completed his M.A. in Physics in June 1996, and will pursue a Ph.D. in Physics at the City University of New York Graduate School. (vi) Richner Erisnor completed his BA in June 1996 and has accepted a teaching position at a New York City public high school (Theodore Roosevelt HS, in the Bronx) with a large minority student population. Mr. Erisnor is very enthusiastic about helping us to recruit future students for our undergraduate program. (vi) Sophia Suarez-Gustave spent a research internship summer at Los Alamos National Lab and begins work on her MA starting this Fall.

In the spring of 1995, we obtained internal funding from the CUNY Central Office to recruit faculty (through teaching release time) and students (through stipends) from affiliated community colleges into our research program. Since the summer of 1995, two chemistry professors (Drs. Stan Bajue and John Flowers) and two minority students (Georgia Burke and Manasse PetitFrere), all from Medgar Evers College in Brooklyn, have worked in the lab. The internal funding was made possible largely due to having had an established program funded by this ARO Grant. We are now expanding these outreach efforts to other community college campuses.

Future Research Opportunities Related to this Grant

Besides scientific progress in lithium battery research described above, this *Infrastructure Grant* has paved the way for continued development of spectroscopic techniques, interaction with industry and training of students, including members of under-represented minorities. In particular, two competitive federal grants have recently been awarded, based on expertise and facilities developed, in large part, due to the ARO funding. The first, beginning in June 1996 is Joint Venture (JOVE) Program with NASA, which provides travel, equipment, supplies and student and summer salary in connection with a scientific collaboration with one of the NASA centers. In our case, we are collaborating with Dr. Jerry Halpert of the Jet Propulsion Laboratory in Pasadena. Dr. Halpert heads the satellite and space probe power sources program, and the research focuses on development and evaluation of new materials for light-weight batteries and fuel cells.

We have also just been awarded a competitive three-year grant from the Chemical Sciences Branch of the Basic Energy Research Division of the Department of Energy. In addition to continuing the efforts previously supported by ARO, this program will support the expansion and development of x-ray synchrotron radiation spectroscopies (e.g. EXAFS and NEXAFS) in battery materials research.